

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-144129

(43)Date of publication of application : 26.05.2000

(51)Int.Cl.

C09K 11/64

(21)Application number : 10-332056

(71)Applicant : AGENCY OF IND SCIENCE & TECHNOL

(22)Date of filing : 06.11.1998

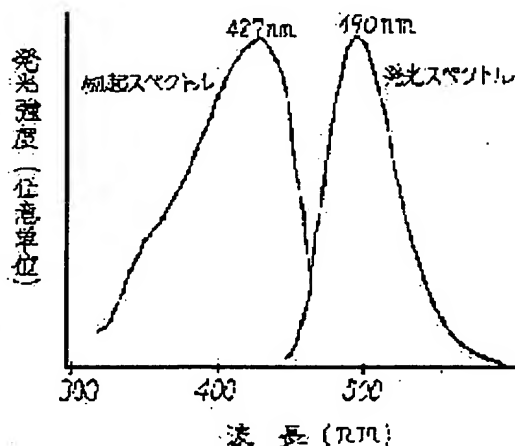
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(54) PHOSPHORESCENT MATERIAL CAPABLE OF BEING EXCITED WITH VISIBLE LIGHT AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an excellent phosphorescent material having high brightness and afterglow for a long time, capable of being excited with visible light, and capable of resisting to outdoor employment for a long period.

SOLUTION: This phosphorescent material is obtained by adding Eu as an activator and at least one element selected from Ti, Zr, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, Ta, W, Bi, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu as a coactivator to a compound of the formula: MA14O7 (M is at least one metal element selected from the group consisting of Mg, Ca, Sr and Ba) as a matrix material. The phosphorescent material can be excited with visible light, has higher luminance than commercial products, and exhibits superafterglow.



LEGAL STATUS

[Date of request for examination] 06.11.1998

[Date of sending the examiner's decision of rejection] 13.06.2000

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision]

of rejection]

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CLAIMS

[Claim(s)]

[Claim 1] MAI 407 The compound (however, at least one or more metallic elements chosen from the group which M becomes from Mg, calcium, Sr, and Ba) expressed is used as a parent ingredient. It adds. the metallic element which expresses Eu with M as an activator -- receiving -- less than [more than 0.0001mol%20mol%] -- as a coactivator further The transition metals of Ti, Zr, V, Cr, Mn, Fe, Co, nickel, Cu, Zn, Nb, Mo, Ta, W, and Bi, And at least one or more elements in the rare earth of La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu the metallic element expressed with M -- receiving -- less than [more than 0.0001mol%20mol%] -- the phosphorescent materials excited by the light characterized by adding.

[Claim 2] SrAl 407 the compound expressed -- a parent ingredient -- carrying out -- as an activator -- Eu -- Sr -- receiving -- less than [more than 0.0001mol%20mol%] -- adding -- further -- as a coactivator -- Dy -- Sr -- receiving -- less than [more than 0.0001mol% 20mol%] -- phosphorescent materials excited by the light characterized by adding.

[Claim 3] CaAl 407 the compound expressed -- a parent ingredient -- carrying out -- as an activator -- Eu -- calcium -- receiving -- less than [more than 0.0001mol%20mol%] -- adding -- further -- as a coactivator -- at least one or more of Nb and D(ies) -- calcium -- receiving -- less than [more than 0.0001mol%10mol%] -- phosphorescent materials excited by the light characterized by adding.

[Claim 4] MAI 407 The compound (however, at least one or more metallic elements chosen from the group which M becomes from Mg, calcium, Sr, and Ba) expressed is used as a parent ingredient. the metallic element which expresses Eu with M as an activator -- receiving -- less than [more than 0.0001mol%20mol%], while adding As a coactivator, the transition metals of Ti, Zr, V, Cr, Mn, Fe, Co, nickel, Cu, Zn, Nb, Mo, Ta, W, and Bi, And at least one or more elements in the rare earth of La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu the metallic element expressed with M -- receiving -- less than [more than 0.0001mol%20mol%] -- the manufacture approach of the phosphorescent materials excited by the light characterized by calcinating at 800-1700 degrees C in reducing atmosphere after adding and mixing.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is excited by the light and relates to the new phosphorescent materials which have the afterglow nature and the high brightness of long duration extremely, and its manufacture approach.

[0002]

[Description of the Prior Art] Conventionally, as phosphorescent materials, CaS:Bi and sulfide fluorescent substances, such as ZnS:Cu , are known well. However, these sulfide fluorescent substances are chemically unstable, there are many troubles in respect of [such as being inferior also to lightfastness,] practical use, and use on the outdoors is difficult, then, SrAl 2O_3 : Eu, Dy, and Sr_4 aluminum 14O_{25} : Eu, Dy, or CaAl 2O_3 : Oxide phosphorescent materials, such as Eu and Nd, were developed and it has been greatly improved to chemical stability or lightfastness. However, these phosphorescent materials have the need of being excited by the ultraviolet rays of high energy, and have the problem of being hard to be excited, in the light which occupies many of sunlight. Moreover, in order to expand the use field of phosphorescent materials, the present condition is the afterglow nature of the further long duration, and that high brightness is called for.

[0003]

[Problem(s) to be Solved by the Invention] Compared with commercial oxide system phosphorescent materials, this invention has the afterglow nature and the high brightness of long duration far, and it is possible to make it excite by the low light of energy moreover, and it aims at offer of the outstanding phosphorescent materials which have the lightfastness which can be equal also to use on the outdoors over a long period of time, and its manufacture approach.

[0004]

[Means for Solving the Problem] The phosphorescent materials of this invention for solving the above-mentioned technical problem MAI 407 The compound however, at least one or more metallic elements chosen from the group which M becomes from Mg, calcium, Sr, and Ba) expressed is used as a parent ingredient. As an activator it adds, the metallic element which expresses Eu with M — receiving — less than [more than $0.0001\text{mol}\%20\text{mol}\%$] — more — desirable — less than [10mol%] — as a coactivator further The transition metals of Ti, Zr, V, Cr, Mn, Fe, Co, nickel, Cu, Zn, Nb, Mo, Ta, W, and Bi, and the metallic element which expresses at least one or more elements in the rare earth of La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu with M — receiving — less than [more than $0.0001\text{mol}\%20\text{mol}\%$] — it is characterized by adding.

[0005] the above-mentioned phosphorescent materials — SrAl 4O_7 the case where use the compound expressed as a parent ingredient and Eu is added as an activator — as a coactivator — Dy — suitable — this case — Eu as an activator — less than [more than $0.01\text{mol}\%1\text{mol}\%$] — adding — Dy of a coactivator — less than [more than $0.01\text{mol}\%1\text{mol}\%$] — adding is more suitable, moreover, CaAl 4O_7 the case where use the compound expressed as a parent ingredient and Eu is added as an activator — as a coactivator — Nb or Dy — suitable — this case — Eu as an activator — less than [more than $0.01\text{mol}\%1\text{mol}\%$] — adding — Nb or Dy of a

coactivator — less than [more than $0.01\text{mol}\%1\text{mol}\%$] — adding is suitable for a twist. [0006] Furthermore, the manufacture approach of the phosphorescent materials of this invention MAI 407 the metallic element which uses the compound expressed as a parent ingredient and expresses Eu with M as an activator — receiving — less than [more than $0.0001\text{mol}\%20\text{mol}\%$], while adding As a coactivator, the transition metals of Ti, Zr, V, Cr, Mn, Fe, Co, nickel, Cu, Zn, Nb, Mo, Ta, W, and Bi, And at least one or more elements in the rare earth of La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu the metallic element expressed with M — receiving — less than [more than $0.0001\text{mol}\%20\text{mol}\%$] — after adding and mixing, it is characterized by calcinating at $800\text{--}1700$ degrees C in reducing atmosphere. [0007] It sets to the above-mentioned manufacture approach, and is SrAl 4O_7 . When using the compound expressed as a parent ingredient, adding Eu as an activator and adding Dy as a coactivator, the approach of calcinating at 1300 degrees C in reducing atmosphere ($\text{Ar}+\text{5}\% \text{H}_2$, 1 l/min) for 4 hours is suitable. Moreover, CaAl 4O_7 When using the compound expressed as a parent ingredient, adding Eu as an activator and adding Nb or Dy as a coactivator, the approach of calcinating at 1300 degrees C in reducing atmosphere ($\text{Ar}+\text{5}\% \text{H}_2$, 1 l/min) for 4 hours is suitable.

[0008] According to the phosphorescent materials and its manufacture approach of such this invention, compared with commercial oxide system phosphorescent materials, it has prolonged afterglow nature and prolonged high brightness far, and it is possible to make it excite by the light moreover, and the outstanding phosphorescent materials which have the lightfastness which can be equal also to use on the outdoors over a long period of time can be obtained.

[0009]

[Embodiment of the Invention] Although the phosphorescent materials of this invention add and constitute an activator and a coactivator into a parent ingredient, a parent ingredient is MAI 407. It chooses from from among the ingredients which consist of a compound (however, at least one or more metallic elements chosen from the group which M becomes from Mg, calcium, Sr, and Ba) expressed. Although it turns out that the afterglow nature and the brightness at the time of using them are high compared with other matter, it is SrAl 4O_7 also among them. Or CaAl 4O_7 it is especially suitable.

[0010] Moreover, if an activator and a coactivator are added into the above-mentioned parent ingredient, afterglow nature and brightness can be raised by leaps and bounds. In order to dope an activator and a coactivator, after often mixing the ingredient used as an activator and a coactivator with a parent ingredient in the form of an oxide or a carbonate, acetate, and a nitrate, it is attained by calcinating more than for 30 minutes at a $800\text{--}1700\text{--degree C}$ elevated temperature in reducing atmosphere, moreover, flux, such as a boric acid or boron oxide, — less than [more than $0.1\text{mol}\%20\text{mol}\%$] — afterglow nature and brightness can be raised by adding.

[0011] As an ingredient used as a coactivator, using Eu as an ingredient used as an activator The transition metals of Ti, Zr, V, Cr, Mn, Fe, Co, nickel, Cu, Zn, Nb, Mo, Ta, W, and Bi, And although one kind or the element beyond it of the rare earth of La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu can be used, the optimal coactivator changes with presentations of a parent ingredient. For example, a parent ingredient is SrAl 4O_7 : When it is Eu, Dy is effective as a coactivator, and it is CaAl 4O_7 : In being Eu, Nd or Dy is suitable.

[0012] The addition of the ingredient used as an activator and a coactivator can be chosen in [0.0001–20 mol %] to the metallic element expressed with M. In not filling it to $0.0001\text{--mol}\%$, afterglow nature and brightness are inadequate, and on the other hand, if it becomes more than $20\text{mol}\%$, it becomes impossible to maintain the crystal structure of a parent ingredient, afterglow nature and brightness fall, and it is not suitable for practical use.

[0013] In addition, it sets to this invention and is MAI 407. In the parent ingredient expressed Even if the metallic elements equivalent to M are which at least one or more metallic elements chosen from Mg, calcium, Sr, and Ba, as an activator Eu as a coactivator At least one or more elements in said various kinds of transition metals and various kinds of rare earth can be chosen as arbitration, and it can add. Or as a coactivator, among said various kinds of transition metals and/or various kinds of rare earth, at least one or more elements within the limits limited to arbitration can be chosen as arbitration, and it can add.

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[0014]

[Example] The example of this invention is shown below. The powder sample was prepared in order to investigate the afterglow nature of the phosphorescent materials concerning this invention and brightness, and an excitation spectrum. A sample offering powder sample is SrAl 4O_7 which is a parent ingredient. After adding $0.7\text{--mol}\%$ of Eu used as an activator, and $0.3\text{--mol}\%$ of Dy used as a coactivator and calcinating it at 1300 degrees C among reducing atmosphere ($\text{Ar}+\text{H}_2$, 5%) for 4 hours, it grinds and considers as phosphorescent-materials powder.

[0015] The above-mentioned excitation spectrum and above-mentioned emission spectrum of a powder sample are shown in drawing 1. The peak wavelength of drawing to an excitation spectrum is 427nm , and being excited by the light is clear. This SrAl 2O_4 : The result of having measured the afterglow nature of Eu and Dy fluorescent substance as compared with the afterglow nature of the aluminate compound phosphorescent materials (Nemoto [& Co., Ltd.] make: name-of-article N noctilucence (RUMINOBA)) of a commercial item is shown in drawing 2. Measurement of the decay characteristic irradiates ultraviolet rays (wavelength: 365nm) for 10 minutes at 1.00g of fluorescent substance powder, and measures afterglow after that using a photo multiplier. SrAl 4O_7 which is a sample offering powder sample so that clearly from drawing 2: The brightness of Eu and Dy fluorescent substance is high, and the attenuation is also looser than a commercial item.

[0016] Furthermore, this SrAl 4O_7 : The result of having investigated the thermoluminescence property (glow curve) from the room temperature at the time of carrying out the luminous stimulus of Eu and the Dy fluorescent substance to 250 degrees C is shown in drawing 3. The thermoluminescence of this fluorescent substance has a peak (85 degrees C and 166 degrees C), there are more amounts of luminescence than the phosphorescent materials of a commercial item, and this drawing shows that a peak is also in an elevated-temperature side. From this to SrAl 4O_7 : It is thought that it had high brightness, the deep trapping level enlarged the time constant of afterglow, and Eu and Dy fluorescent substance have contributed it to phosphorescent [covering long duration].

[0017]

[Effect of the Invention] According to this invention, as explained in full detail above, it is excited by the light, and brightness is high and the new phosphorescent materials which show super-afterglow nature, and its manufacture approach can be acquired. Moreover, when brightness increased, the large application of the possibility of use as a completely new emitter etc. is expectable.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing_1] It is the graph which shows the excitation spectrum and emission spectrum of the sample (SrAl4 O7 : Eu, Dy) concerning this invention.

[Drawing_2] It is the graph which shows the decay characteristic of the sample (SrAl4 O7 : Eu, Dy) concerning this invention, and commercial item phosphorescent materials.

[Drawing_3] It is the graph which shows the thermoluminescence property (glow curve) of a sample (SrAl4 O7 : Eu, Dy) and commercial item phosphorescent materials concerning this invention.

[Translation done.]